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Spectroscopic investigation of local molecular dynamics in liquid crystals II. Polymers

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Invited Article

Spectroscopic investigation of local molecular dynamics in liquid crystals

II. Polymers

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In the analysis of spectroscopic data from liquid crystals consisting of either small molecules or polymer chains, it is essential that account be taken of some particular features due to the oriented nature of the phases investigated. For liquid crystal polymers some specific additional problems arise, such as the difficulties in orienting main-chain liquid crystal polymers, the occurrence of the glass-liquid transition and secondary transitions. These questions are first discussed, then the studies performed using ^{2}H and ^{13}C N.M.R., E.S.R. and dielectric relaxation on both side-chain and main-chain liquid crystal polymers are presented.

1. Introduction

In an earlier article [1] we have reviewed various spectroscopic techniques ^{1}H, ^{13}C and ^{2}H N.M.R., E.S.R. and dielectric relaxation. Particular attention was paid to the frequency range of the molecular motions which can be investigated with each technique. The particular features related to the oriented nature of liquid crystal phases were developed and examples of studies on small molecular liquid crystals were presented.

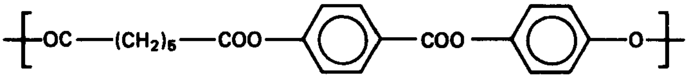
This article deals with the spectroscopic analysis of the local motions of liquid crystal polymers with mesogenic units either in the main chain or in the side chains. Due to the polymeric nature of the systems considered, some specific problems arise concerning the orientation of these materials and the occurrence of a glass-liquid transition. These features are discussed first, then the main results obtained on local dynamics in side-chain and main-chain liquid crystal polymers are described in successive sections.

2. Orientation of liquid crystal polymers

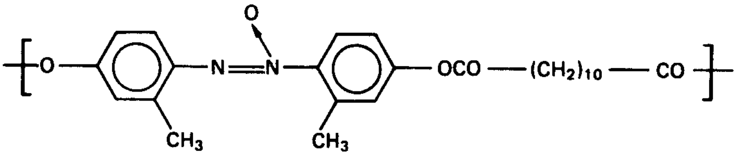
Ordinary bulk polymers in the melt exhibit a flow viscosity which increases as the 3·5 power of their molecular weight. Although the exponent is not yet known for liquid crystal polymers, there is clear evidence that there is a high molecular weight dependence of the mean flow viscosity. This point is very important when looking at the orientational behaviour of different polymers or samples. Unfortunately, very few molecular weights of such polymers have been determined and the inherent viscosity,

η_{inh}, is frequently the only information available. In principle liquid crystal polymers could be oriented and organized in single-domain samples by the same procedures as for low molar mass liquid crystals, i.e. by applying magnetic or electric fields. In practice, however, problems arise due to the high viscosity of these materials, in particular when main chain liquid crystal polymers are considered. For a review, see [2].

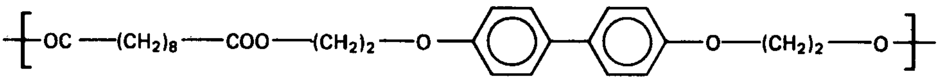
Orientation in a magnetic field at a temperature close to the clearing point has been obtained for nematic main-chain liquid crystal polymers. For example, a polyester having the repeat unit



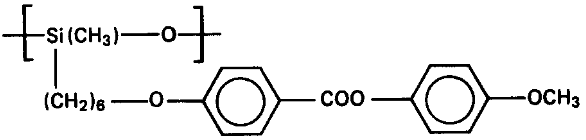
has been oriented parallel to a 0·3 T field [3]. A director order parameter $S_d = 0{\cdot}64$ has been achieved after 24 hours for a sample having $\eta_{inh} = 0{\cdot}29$ dl/g but a sample with $\eta_{inh} = 0{\cdot}54$ dl/g only reached $S_d = 0{\cdot}54$. Similarly, a copolyester synthesized from terephthalic acid and an equimolar mixture of methylhydroquinone and pyrocatechol has been oriented in a field larger than 0·6 T, the orientation time being less than 2 min for a sample of molecular weight 200 000 [4]. Very large values of S_d, ranging from 0·72 to 0·88, have been achieved in a 1 T field [5] with a polymer having the repeat unit



At the other extreme, no orientation was obtained in a field as high as 16 T for a polymer with the structure [6]

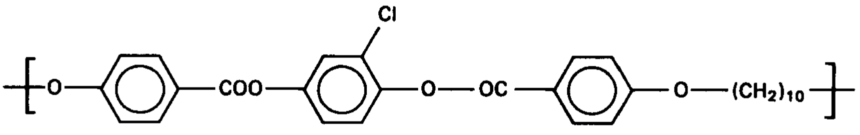


It seems easier to orient the mesomorphic units of side-chain liquid crystal polymers, as has been done [7] with a siloxane polymer of repeat unit



However, it should be noted that the observed relaxation time is longer for the polymer than for the model compound, in spite of the high flexibility of the siloxane linkage.

Similar behaviour is encountered for orientation in electric fields. However, depending on their chemical structure, the mesogenic units can have a positive or negative dielectric anisotropy. In the latter case, this leads to a two dimensional distribution of the director axes perpendicular to the applied electric field. Such a situation is found with ester groups, and, for example with the polyester having the repeat unit

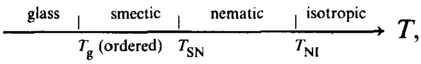


an order parameter $S_d = -0{\cdot}5$ is achieved in an electric field ($E = 50\,\mathrm{kV/cm}$, $\nu = 50\,\mathrm{kHz}$) whereas a 7·0 T magnetic field yields $S_d = 1{\cdot}0$ [8]. Combined effects of perpendicular electric and magnetic fields have been used to orient an ester side-chain liquid crystal polymer with positive diamagnetic and negative dielectric anisotropy [9].

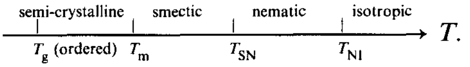
3. Glass–liquid transition and secondary transitions

If polymers do not possess sufficiently high chemical and stereochemical regularity, they are not able to crystallize and on decreasing the temperature they undergo a transition from a highly viscous liquid to a solid glass, called the glass transition. Even for polymers with a high chemical regularity, as for example high density polyethylene, the material never achieves a fully crystalline state and amorphous regions coexist with crystalline regions (semi-crystalline polymers). These amorphous parts of the bulk polymer undergo a glass transition.

The same situation is encountered with liquid crystal polymers. Depending on their chemical structure semi-crystalline states may be obtained or not. However, due to the occurrence for these polymers of nematic and/or smectic phases, either the whole material or only the non-crystalline parts of the material will yield an ordered glassy state which is characterized by a glass transition temperature, T_g (ordered). Such a situation is achieved by cooling the polymer slowly from the high temperature isotropic state. Of course, if no orientation procedure has been applied, a multidomain sample is obtained. The resulting structures in the two cases of non-crystalline and semi-crystalline polymers are shown schematically in figure 1. If it is assumed that a nematic phase and one smectic phase occur, the observed transitions would be for the non-crystalline case



for the semi-crystalline case



When a very rapid quenching is applied from the isotropic phase, some regions may retain in the rigid solid the disordered structure of the isotropic state, whereas other regions undergo the mesophase transitions leading to an ordered glassy state. As polymer segments are less constrained in the disordered glass than in the ordered one, samples prepared under such conditions exhibit two glass transition temperatures, the transition occurring at the lower temperature corresponding to the regions where the isotropic structure has been preserved.

Before considering the effect of the occurrence of a glass transition on the assignment of all the transitions observed by spectroscopic techniques, it is worthwhile

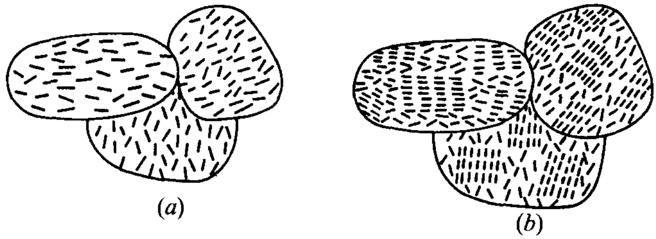


Figure 1. Schematic representation of a multi-domain sample for (*a*) a glassy nematic polymer, (*b*) a semi-crystalline nematic polymer. Only the mesogenic groups are represented.

recalling that mesophase transitions are thermodynamic transitions, and as such the temperatures at which they are observed do not depend on the frequency of the technique used for their investigation (calorimetry techniques correspond to frequencies around 1 Hz, spectroscopic techniques cover various frequency ranges as mentioned in [1] §3). Conversely the glass transition observed experimentally is controlled by the kinetics of the structural changes of the material, thus it has a kinetic nature and the temperature at which it is observed depends on the frequency of the investigating technique. Typically, the glass transition temperature is shifted upwards by 5°C to 10°C when the measurement frequency is increased by a factor of 10. A commonly used relationship to account quantitatively for the glass transition temperature shift is the so-called W.L.F. equation [10]

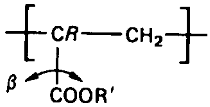
$$\log(f_2/f_1) = -A[T_g(f_1) - T_g(f_2)]/[B + (T_g(f_1) - T_g(f_2))],$$

where $T_g(f_1)$, $T_g(f_2)$ are the glass transition temperatures observed at frequencies f_1 and f_2, respectively, and A and B are constants which depend slightly on the polymer but can be assumed as universal, to a first approximation. This relationship can be derived from the free volume theory. It describes a non-arrhenian behaviour of the molecular phenomena responsible for the glass transition. It is worth noting that the W.L.F. equation is equivalent to the empirical Vogel, Fulcher, Tamman equation

$$f = A' \exp(-C/(T - T_\infty)),$$

where T_∞ is a characteristic temperature of the material.

In addition to the glass transition (α), most polymers in the solid state exhibit secondary transitions (β, γ, etc.) which correspond to the motions of groups in the side chain or the main chain, such as for example the β transition observed in polyacrylates (R = H) or methacrylates (R = CH_3)



$$-\!\left[\begin{array}{c}CR\\ \overset{\beta}{|}\\ COOR'\end{array}\!\!-\!CH_2\right]\!-$$

which is assigned to rotational motion of the ester group around its linkage to the main chain. These secondary transitions are characterized by a frequency dependence which corresponds to an arrhenian activated process. The various transitions undergone by a bulk polymer are usually represented in a relaxation map, as shown in figure 2 (*a*), where $\log f$ is plotted against $1/T$ for each transition. At high temperature and high frequencies, the glass transition and β transition may merge.

For a liquid crystal polymer, in addition to the secondary and glass transitions, mesophase transitions occur which correspond to temperatures independent of frequency, as represented in figure 2 (*b*) for a non-crystalline system with a nematic and a smectic phase. Thus, for low frequency measurements, on increasing temperature the following transitions appear: γ, β, glass transition, smectic–nematic and nematic–isotropic. At higher frequencies, but lower than the frequency, f_a, where $T_g(f_a)$ is equal to T_{SN}, the same behaviour is observed and, in particular, the glass transition associated with the ordered glassy state (in figure 2 it would be a smectic glassy state) can be detected. At frequencies higher than f_a (for example f_b in figure 2 (*b*)) molecular motions in the isotropic, nematic, smectic liquid phases or solid state can be investigated, but the high frequency glass transition of the smectic glassy state no longer exists because the smectic–nematic transition will change the original smectic structural

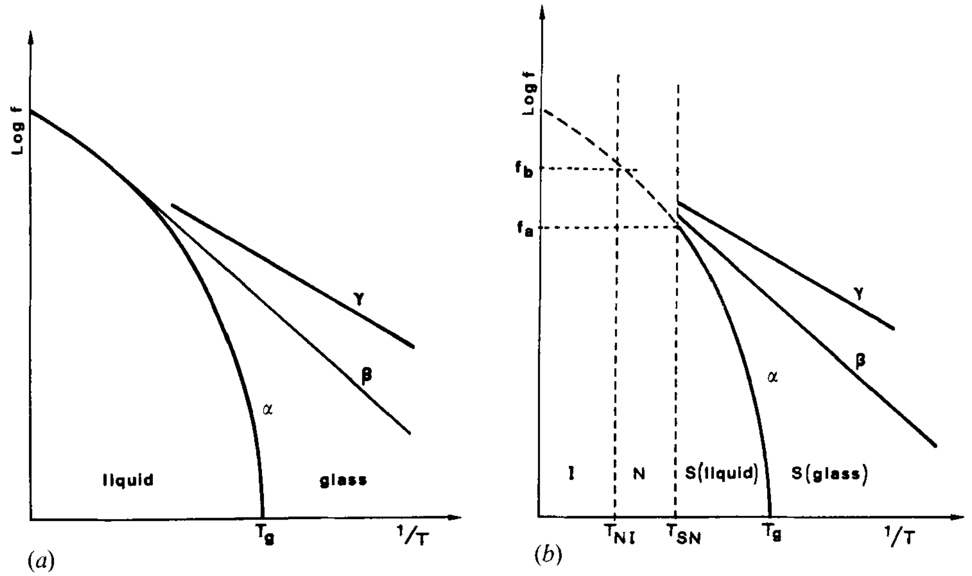


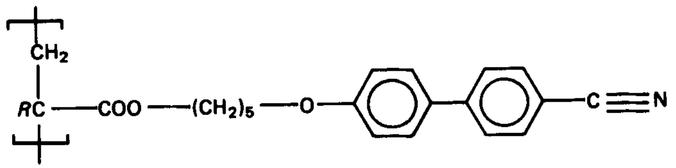
Figure 2. Schematic relaxation maps for (*a*) an ordinary amorphous polymer and (*b*) a non-crystalline liquid crystal polymer with smectic and nematic phases.

arrangement of the polymer segments. These features are very important for assigning the various transitions observed using spectroscopic techniques. In particular, a transition occurring at high frequency in a temperature range where the glass transition is observed by calorimetry experiments does not correspond to the glass transition process but to secondary relaxations (β, γ, etc.).

Finally, it is clear from these considerations that to study the molecular processes involved in the glass transition of the ordered, glassy state using a spectroscopic technique operating at a frequency, f, it is essential that the mesophase found in the glassy state remains till a temperature higher than $T_g(f)$. Typically, to perform such a study at 10^5 Hz, it is necessary that the polymer does not undergo any mesophase transition at a temperature lower than T_g (calorimetry) + 50°C (at 10^8 Hz, it would become T_g (calorimetry) + 80°C).

4. Local dynamics in side-chain liquid crystal polymers

Dielectric relaxation experiments have been performed on various side-chain liquid crystal polymers. Thus, investigations of the dynamic behaviour in the mesophase and the isotropic phase have been carried out [11–14] on polymers with the repeat units



later samples with R = H, CH_3 will be referred to as PACB and PMACB, respectively. The phase transitions determined from calorimetry experiments are

$$\text{PACB}:\text{glass} \xleftrightarrow{313\,\text{K}} \text{N} \xleftrightarrow{390\,\text{K}} \text{I},$$

$$\text{PMACB}:\text{glass} \xleftrightarrow{333\,\text{K}} \text{S} \xleftrightarrow{397\,\text{K}} \text{I}.$$

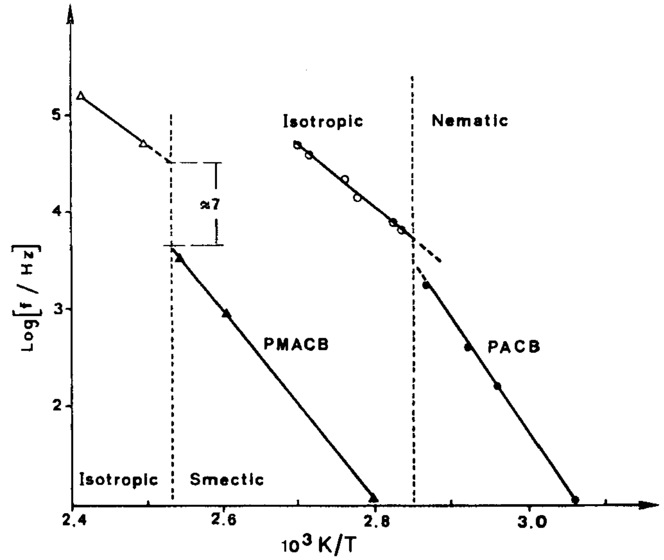


Figure 3. Log f versus $1/T$ for PACB and PMACB in mesomorphic and isotropic states (after [12]).

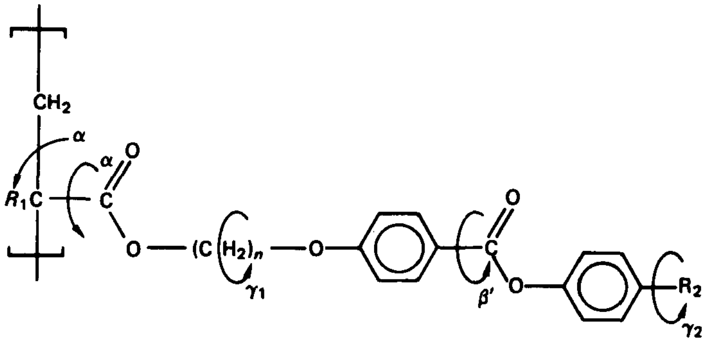
Measurements on multi-domain samples yield the temperature dependence of the frequency at the maximum of ε'' shown in figure 3. For PACB a small increase in frequency occurs at the nematic–isotropic transition whereas it is three times larger at the smectic–isotropic transition of PMACB. A decrease in the apparent activation energy is observed in both cases between the mesophase and the isotropic state. For PACB, a partially oriented sample was obtained by applying an electric field and relaxation measurements were then performed with the oscillating electric field parallel or perpendicular to the director. In addition to the low frequency absorption, in both cases a high frequency relaxation exists. For example, at 321·9 K, the frequency values are $F_{\parallel 1} = 1{\cdot}7$ Hz, $F_{\parallel 2} \approx 200$ Hz and $F_{\perp 1} = 2{\cdot}5$ Hz, $F_{\perp 2} \approx 200$ Hz but the relaxation amplitude is only half as large for the perpendicular as for the parallel arrangement. From the data reported in table 1 it is clear that the reorientation of the mesogenic group around the main chain, corresponding to the parallel relaxation, is about 100 times slower than the rotational motion of the side chain around its long axis. The relaxation frequency measured on a multi-domain sample mainly reflects the reorientation motion of the mesogenic group. It is interesting to compare these results with the correlation times observed on the low molar mass liquid crystal 4-*n*-heptyl-4-cyano biphenyl (7 CB) and shown in figure 13 of [1]. It appears that the chain backbone slows down the motions of the cyanobiphenyl group considerably, for

Table 1. Relaxation frequencies for partially oriented ($F_{\parallel 1}$, $F_{\perp 2}$) and isotropic multi-domain samples [13].

T K	321·9	331	342·2	353·7
$F_{\parallel 1}$ Hz	1·7	28	290	2100
$F_{\perp 2}$ Hz	200	2000	20 000	≃ 150 000
F Hz	7	110	800	5000

reorientational motion about an axis perpendicular to the biphenyl axis as well as for rotational motion about the molecular long axis.

A series of side-chain polymers has recently been studied by dielectric relaxation in the frequency range 10^2–10^7 Hz for both solid and liquid states [15, 16]. The general formula of the repeating unit is



where R_1 = H or CH_3, n = 2 or 6 and R_2 = CN, OCH_3 or $O(CH_2)_3CH_3$. The samples were not oriented. Depending on the chemical structure, several transitions have been observed in the solid state; they are represented schematically in the relaxation map shown in figure 4. The β' transition is observed at the same position regardless of the nature of R_1 and R_2 and of the length of the spacer; its apparent activation energy is 50 kJ mol^{-1}. Such behaviour suggests that this transition should be assigned to an internal motion of the mesogenic group. However, when compared to the β relaxations of polymethacrylate (PMAD) and polyacrylate derivatives (PAD) which are attributed to a rotational motion of the ester group relative to the chain backbone, this β' relaxation appears very different for several reasons [17]; first at a given frequency, the β transition of PAD occurs at much lower temperatures than that of PMAD (the temperature shift is about 120 K) and secondly the apparent activation energy of the β transition is about 84 kJ mol^{-1} for PMAD and 42 kJ mol^{-1} for PAD. The fact that the relaxation associated with the rotation of the ester group next to the chain backbone is not found in these side-chain liquid crystal polymers could originate from the large decrease in the amplitude of the β relaxation observed in PMAD

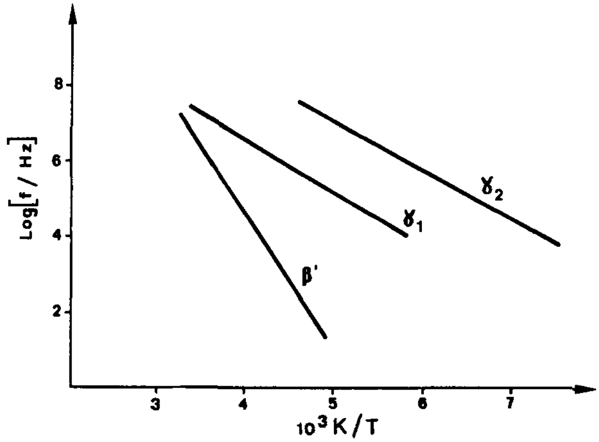


Figure 4 Typical dielectric relaxations in the solid state.

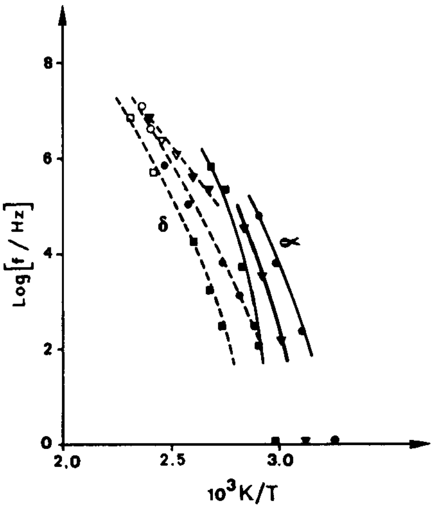


Figure 5. Dielectric relaxations in the liquid state. Log *f* versus $1/T$. α relaxation corresponds to solid lines and δ relaxation to dotted lines. Polymer samples: □, R_1 = H, $n = 2$, R_2 = OCH$_3$; ○, R_1 = H, $n = 6$, R_2 = CN; ▽, R_1 = CH$_3$, $n = 6$, R_2 = OCH$_3$ (filled symbols: nematic or smectic phase, pen symbols: isotropic phase) (after [16]).

when the size of the substituent is increased. The γ_1 transition is only observed for the longer spacer ($n = 6$) and does not depend on R_1 and R_2; its apparent activation energy is 35 ± 10 kJ mol^{-1}. It has been assigned to motions initiated by the $(CH_2)_6$ sequence of the side chain becoming dielectrically active because of coupling to the adjacent dipole moments. The γ_2 transition only occurs in polymers with R_2 = OC_4H_9, and consequently corresponds to a motion localized in this sequence. The dielectric relaxations (denoted α) shown in figure 5 for a few compounds are accurately extrapolated to the corresponding calorimetric glass transition temperatures; furthermore some of them exhibit a non-arrhenian behaviour and the frequency depends sensitively on temperature (the mean slope yields typical apparent activation energies in the range 150–350 kJ mol^{-1}). The main chain motions involved in the glass transition are observed in dielectric relaxation since they cause a reorientation of the adjacent ester dipole. Finally, at higher temperature, for polyacrylate compounds (R_1 = H), another dielectric relaxation (denoted δ) is observed both in mesomorphic and isotropic liquid states (see figure 5). Its amplitude is much higher for the CN end group than for OCH$_3$ or OC_4H_9, indicating that it is related to a motion involving some reorientation of the mesogenic unit. Furthermore, comparison with the results reported in table 1 shows that the δ relaxation frequency lies in the same range, so the same molecular mechanism could be responsible for it. It should be noted first that the δ relaxation is very weak for the polyacrylates with a short spacer and secondly is not found for polymethacrylates where only one transition, related to the glass transition, is observed except in the case of $n = 6$ and R_2 = OC_4H_9 where a δ transition occurs. These remarks could support an interpretation of the δ relaxation as a reorientational motion of the mesogenic group perpendicular to the local chain backbone axis which would be facilitated by a more flexible chain backbone (i.e. R_1 = H instead of R_1 = CH$_3$) or a longer spacer. Such a reorientational motion would be similar to that observed in low molar mass liquid crystals, except that in the case of side-chain liquid crystal polymers its frequency is considerably reduced. It

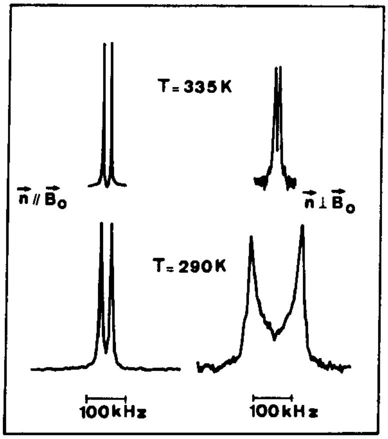


Figure 6. ^{2}H N.M.R. spectra of an oriented smectic phase at 335 K and 290 K with the director **n** parallel (left) and perpendicular (right) to the magnetic field for the polymer sample with R_1 = H, $n = 6$ and R_2 = OCH_3 (after [19]).

does not seem that the frequency of this motion undergoes any discontinuity either at the mesophase transitions or at the clearing temperature.

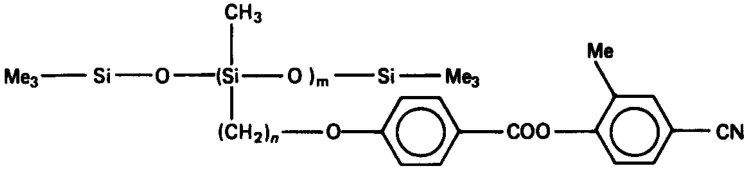
Recent dielectric relaxation studies on the same series of side-chain liquid crystal polymers [18] have confirmed the assignments of δ and α relaxations of the polymer with R_1 = H, $n = 6$ and R_2 = CN. For the polymer with R_1 = H and $n = 2$ a slowing down of about one order of magnitude is observed for the δ process, due to the decrease of flexibility of the mesogenic side group with this short spacer. Such behaviour supports the assignment of the δ relaxation to a reorientational motion of the mesogenic group perpendicular to the local chain backbone axis.

^{2}H N.M.R. studies have been performed on one member of this series, i.e. R_1 = H, $n = 6$ and R_2 = OCH_3 [19, 20]. The terminal phenyl ring was fully deuteriated. The sample was oriented in its nematic phase by the magnetic field (8·5 T) of the N.M.R. spectrometer and an oriented smectic phase was reached by cooling slowly. The phase transition temperatures are

$$\text{glass} \xleftrightarrow{305\,\text{K}} \text{S} \xleftrightarrow{365\,\text{K}} \text{N} \xleftrightarrow{383\,\text{K}} \text{I}.$$

Typical ^{2}H N.M.R. spectra of the smectic phase above T_g (at 335 K) and below T_g (at 290 K) are shown in figure 6, with the director **n** parallel or perpendicular to the magnetic field. In the liquid smectic phase, at 335 K, the rotational motion of the phenyl ring about the direction of order is rapid enough to yield partial averaging of the quadrupolar coupling. On the other hand, below T_g, in the glassy smectic phase, there is an appreciable change in the molecular motion of the mesogenic group, reflected in the substantial broadening of the spectra. For **n** parallel to the magnetic field, however, a single quadrupolar splitting is observed, in spite of the fact that the investigated phenyl ring contains two inequivalent deuterons in the rigid case. This is an indication that restricted motion of the mesogenic group occurs. From a lineshape analysis, it appears that the terminal phenyl ring undergoes 180° rotational jumps in the glassy state with a slight gaussian distribution of rotation angle with a variance of 8°. At 290 K, the jump correlation time is approximately 3×10^{-7} s with an activation energy of 12 kJ mol^{-1}. This 180° phenyl ring jump should be associated with a secondary relaxation.

Dielectric relaxation measurements have recently been performed [21–26] on side-chain liquid crystal polymers with a similar mesogenic group but a siloxane backbone instead of the polyacrylate or polymethacrylate backbone considered previously. The chemical structure was



with $n = 5$, 6 and 8. The phase transition temperatures are

$$n = 5 \quad \text{glass} \xleftrightarrow{275\,\text{K}} \text{N} \xleftrightarrow{325{\cdot}7\,\text{K}} \text{I}$$

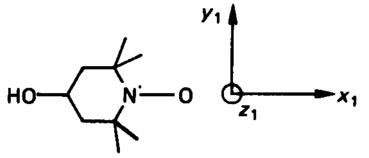
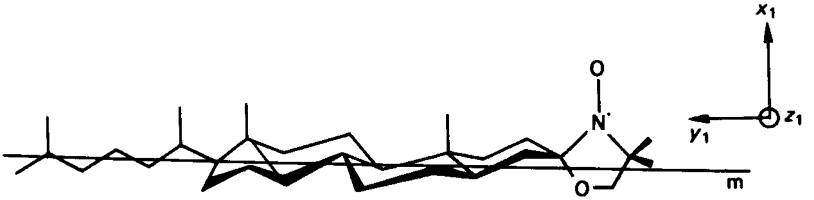
$$n = 6 \quad \text{glass} \xleftrightarrow{275\,\text{K}} \text{N} \xleftrightarrow{319\,\text{K}} \text{I}$$

$$n = 8 \quad \text{glass} \xleftrightarrow{274\,\text{K}} \text{S} \xleftrightarrow{363\,\text{K}} \text{I}.$$

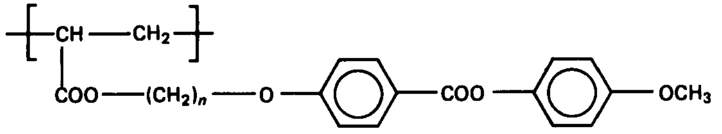
In the three compounds α and δ relaxation processes were observed both in unoriented and aligned samples. However, the relative strength of the α and δ relaxations depends strongly on the degree of alignment. Such a behaviour has been accounted for [23] by considering four relaxation processes which are all active in the case of unoriented samples, but which split into two groups for aligned samples, each group being responsible for the specific relaxation observed with the electric field either parallel or perpendicular to the sample director. The detailed analysis of the experimental data shows that the δ relaxation corresponds to a process involving only the motions of the longitudinal component of the dipole moment of the mesogenic head group. In contrast, the α relaxation involves both the longitudinal and the transverse components of the dipole moment of the mesogenic head group (in spite of the major contribution of the transverse component). The theory predicts also that for a planary-aligned sample only the α relaxation should exist as has been observed [25]. It has to be pointed out that the frequency of the dielectric loss maxima and the width of the relaxations are independent of the degree of alignment of the sample. The temperature dependence of the α and δ relaxation frequencies clearly show that both have contributions resulting from the glass transition of the material, as revealed by their non-arrhenian behaviour and the high values of their apparent activation energies which lie in the range 130–180 kJ mol^{-1}. Such a statement is supported by dielectric studies performed under pressure [27] on two 4-cyano-phenyl benzoate polyacrylates. Finally, it is worth noting that for the compound with $n = 8$, the orientation of the smectic phase is maintained without any ageing at temperatures above the glass transition, showing that the micro-brownian motions of the main chains and the flexible spacers are not able to destroy the previously achieved alignment.

More recent data obtained on side-chain liquid crystal polyacrylates [28] lead to the same conclusions about the contributions of the motions of longitudinal and transverse components of the dipole moment of the mesogenic unit to the δ and α relaxation processes. The assignments of the various dielectric relaxation processes observed in the side-chain liquid crystal polymers have been confirmed on a large series of polyacrylate compounds [29] in which the length of the spacer and the chemical structure of the mesogenic head-groups, have been varied.

Table 2. Acronyms and formulae of the nitroxide probes discussed in the text.

Acronym	Formulae
Tempol	
CSL	

In the field of side-chain liquid crystal polymers, an E.S.R. study has been performed [9, 30] on compounds with the structure



$$-\!\!\left[\mathrm{CH}-\mathrm{CH_2}\right]\!\!-\quad \mathrm{COO}-(\mathrm{CH_2})_n-\mathrm{O}-\mathrm{C_6H_4}-\mathrm{COO}-\mathrm{C_6H_4}-\mathrm{OCH_3}$$

with two spacer lengths ($n = 2$ for P2 and $n = 6$ for P6). The samples had molecular weights in the range 4500–21 000 for P2 and 2500–14 000 for P6. The corresponding phase transitions are

$$\mathrm{P}\ 2a(\bar{\mathrm{M}}_a = 21\,000)\quad \text{glass} \xleftrightarrow{334\,\mathrm{K}} \mathrm{N} \xleftrightarrow{388\,\mathrm{K}} \mathrm{I},$$

$$\mathrm{P}\ 6a(\bar{\mathrm{M}}_n = 14\,000)\quad \text{glass} \xleftrightarrow{302\,\mathrm{K}} \mathrm{S_A} \xleftrightarrow{367\,\mathrm{K}} \mathrm{N} \xleftrightarrow{393\,\mathrm{K}} \mathrm{I}.$$

Oriented samples were obtained by the combined effects of perpendicular magnetic and electric fields. The nitroxide used was the CSL probe (*cf.* table 2) which is rigid and appears to be located exclusively in the side-chain region, as indicated by the measured order parameter. For both polymers the anisotropy coefficients ($N = \tau_{R\perp}/\tau_{R\|}$, where $\tau_{R\perp}$ and $\tau_{R\|}$ are the correlation times for motions around the molecular long and short axes, respectively) are identical and equal to 7 in the isotropic phase and 10 in the nematic and smectic phases. No significant effect due to molecular weight is observed, the temperature dependence of $\tau_{R\|}$ is plotted against $1/T$ in figure 7. It first appears that increasing the spacer length from $n = 2$ to $n = 6$ decreases the correlation times by about one order of magnitude for the isotropic and nematic phases, whereas there is no effect in the glassy state, as we should expect. Only the smectic–nematic transition shows an abrupt change in correlation times. The break in slope observed at a temperature around the calorimetric glass transition should not be assigned to the glass transition phenomena, as has been proposed in [9] since the high frequency E.S.R. measurements should yield a much higher glass

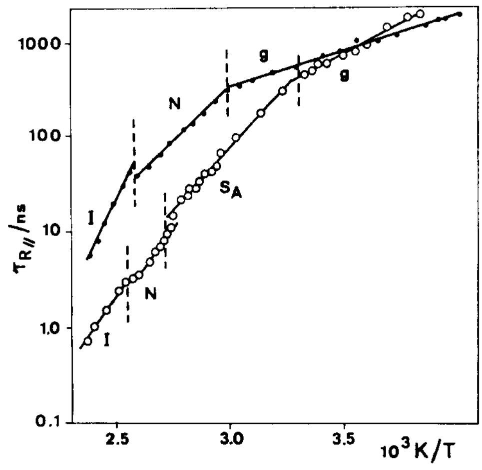
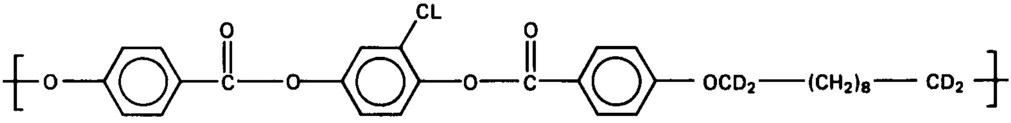


Figure 7. $\tau_{R\parallel}$ versus $1/T$ for CSL in P2*a* (full circles) and P6*a* (open circles) (after [9]).

transition temperature, as previously discussed. More probably such discontinuities reflect the occurrence of a local motion in the E.S.R. frequency range which could be related to a β process. In the absence of complementary experiments (dynamic mechanical studies, dielectric relaxation, N.M.R.) it is not possible to assign this local motion.

5. Local dynamics in main-chain liquid crystal polymers

A ^{2}H N.M.R. study has been performed on a main-chain liquid crystal polymer [31], with the repeat unit



The corresponding transition temperatures are

$$T_g = 303\,\mathrm{K};\quad T_m = 433\,\mathrm{K};\quad \mathrm{N} \xleftrightarrow{553\,\mathrm{K}} \mathrm{I}.$$

The T_1 and T_2 relaxation times have been measured at various temperatures on a sample oriented in the magnetic field (7 T). The analysis includes (i) the intramolecular motion of the CD_2 group due to $t \leftrightarrow g^{\pm}$ jumps and characterized by a correlation time τ_j and (ii) the intermolecular motion of the repeat unit considered as axially symmetric and rigid, undergoing continuous anisotropic diffusion, within an orienting potential, characterized by correlation times $\tau_{R\parallel}$ and $\tau_{R\perp}$ for rotation about the molecular long and short axis, respectively. The temperature dependence of these correlation times is plotted in figure 8. Below the melting point, T_m, the sample is partially crystallized at a rate of about 60 ± 5 per cent, as estimated from the ratio of the rigid to mobile components of the spectra. At the melting point, the $t \leftrightarrow g^{\pm}$ isomerization exhibits two different behaviours. In the crystalline phase (rigid component), the isomerization is reduced by more than two orders of magnitude and the corresponding activation energy is approximately 6·7 kJ mol^{-1}, which is comparable to the values observed in crystalline paraffins. In the amorphous phase, the isomerization process is gradually

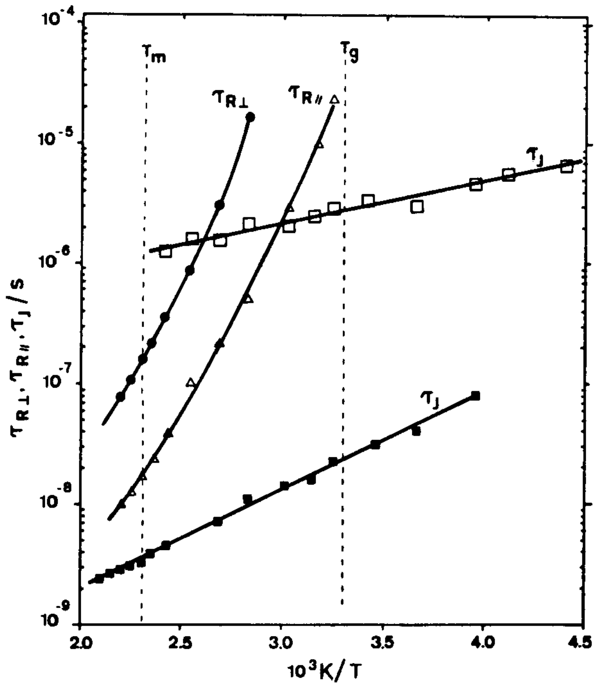
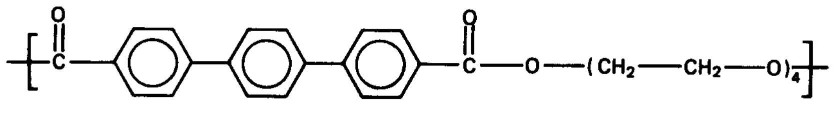


Figure 8. Logarithmic plot of the correlation times τ_j, $\tau_{R\parallel}$ and $\tau_{R\perp}$ versus $1/T$ (after [31]).

slowed with an activation energy of $15{\cdot}9\,\mathrm{kJ\,mol^{-1}}$. This higher value could indicate that the $t \leftrightarrow g$ jumps undergone by the CD_2 groups in the amorphous phase are connected with motions of larger chain units, possibly involving the nearest neighbouring phenyl ring, whereas in the crystalline phase only local jumps of the adjacent CH_2 groups would be involved. It is worth noting that the activation energy in the amorphous phase is comparable to that observed for $\left(\mathrm{CH_2-CH_2-O} \right)$ units in a polyaromatic ester with a similar structure, as described later.

The correlation times of the intermolecular motions of the repeat unit ($\tau_{R\parallel}$ and $\tau_{R\perp}$) in the anisotropic melt, are of the order of 10^{-8} s and 10^{-7} s, respectively. Below the melting point these motions still occur in the amorphous phase and the observed slowing down when reaching the glass transition has the typical feature of non-arrhenian processes encountered in ordinary amorphous polymers, i.e. a temperature dependence of the correlation time which can be described by the W.L.F. equation. The same polymer has been deuteriated in different positions (the central phenyl ring and the four central methylene groups) but the results on the observed dynamics have not yet been published.

Dielectric, ^{13}C N.M.R. [32, 33] and E.S.R. [34] measurements have been carried out on a main-chain liquid crystal polymer with the repeat unit



In the solid state, the investigated samples contain a few isolated regions of disordered (amorphous isotropic) material, dispersed in a semi-crystalline continuum. The various

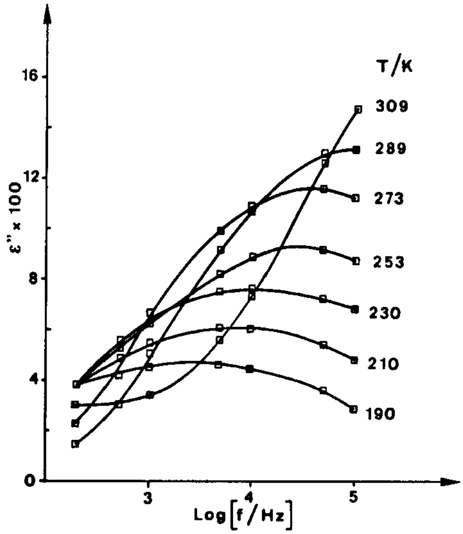


Figure 9. The dielectric loss factor ε″ as a function of frequency for a selection of temperatures (after [33]).

calorimetric transitions are:

$$\text{glass}_{(1)} \xleftrightarrow{233\,\text{K}} \text{glass}_{(2)} \xleftrightarrow{293\,\text{K}} \text{C} \xleftrightarrow{393\,\text{K}} \text{S}_\text{C} \xleftrightarrow{523\,\text{K}} \text{I}.$$

It has not been possible to orient the samples in a 1 T magnetic field and all the experiments have used mesomorphic multi-domain samples. Dielectric relaxation measurements have been performed in the low temperature range and the behaviour of ε″ as a function of log *f* is plotted in figure 9. At 193 K a relaxation process occurs with a small amplitude indicating a limited freedom for the electric dipoles. The absorption peak, with a maximum around 5 × 10^3 Hz, is very broad, which suggests that there is a wide range of local environments for the dipoles and that the environment places great constraints on the motion. A given dipole group can move only in cooperation with that environment, this being a slow process overall. As the temperature is increased, the whole system cooperatively moves faster, narrowing the overall loss of peak. As a consequence, at high enough temperatures a reference group moves in an average environment. From the shift of the maximum of ε″ with temperature, an apparent activation energy of 16 kJ mol^{-1} is deduced. It is worth noting that in the same frequency–temperature range a similar relaxation is observed in poly aliphatic ethers which has been assigned to a local twisting motion.

The motions involved in this relaxation process have been analysed by ^{13}C solid state high resolution N.M.R. at 298 K. It appears that at the frequency involved in the relaxation methods used, i.e. 10^5 Hz, the carbonyl group and the nearest CH_2 group have a rigid behaviour whereas the next-nearest CH_2 group undergoes oscillations on the valence cone of approximately 20° about one equilibrium conformation. The following CH_2 group performs oscillations of large amplitude or more likely jumps between two equilibrium conformations. Several nitroxide probes of different sizes have been studied and it has been shown that in the very slow motional regime ($\tau \geqslant 10^{-8}$ s) small probes such as Tempol (*cf.* table 2) undergo jump diffusion motions whereas large probes have a brownian rotational diffusion. Characteristic

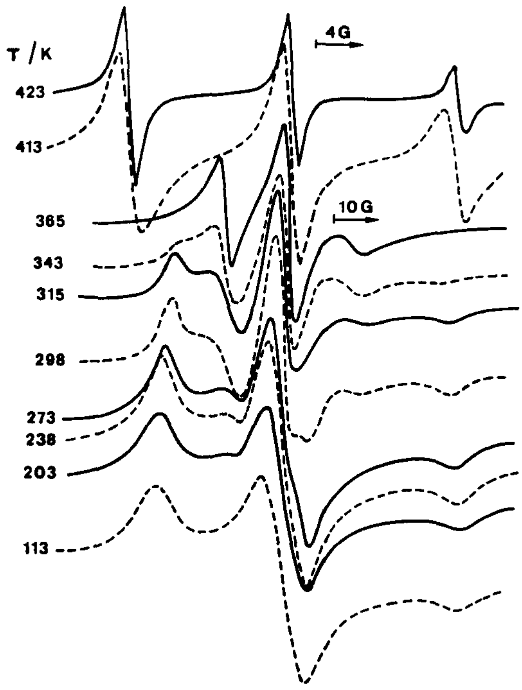


Figure 10. E.S.R. spectra of the Tempol probe for a variety of temperatures (after [33]).

E.S.R. spectra obtained for Tempol in the temperature range 113 K–423 K are shown in figure 10. At 203 K the separation of the outer hyperfine extrema decreases slightly with increasing temperature, indicating the onset of slow motion of the spin probe due to local main chain motions. These motions are the same as those observed by dielectric and ^{13}C relaxation and assigned previously to conformational jumps of the bonds of the central part of the aliphatic ether sequences in the liquid crystal polymer chain. In order to obtain information on the correlation times of motions performed by the nitroxide probes over the whole temperature range investigated, E.S.R. spectra have been treated assuming an isotropic reorientation. Resulting isotropic correlation times, τ_{iso}, for Tempol are plotted against $1/T$ in figure 11. It can readily be seen that τ_{iso} does not fit an arrhenian type expression over the whole temperature range. From 203 K to 273 K the Tempol probe reflects the conformational jumps of the aliphatic ether sequences, proving that the probe molecules would be preferentially localized in the interlayer regions of the smectic C phase. A change in the slope of the arrhenian plot for τ_{iso} is observed around 273 K, corresponding to an increase in the probe mobility. Furthermore complex E.S.R. spectra are observed (see figure 10), which can be resolved into a mobile component and a solid state component. The same behaviour is found for a similar polyester with 10 ethylene oxide units instead of 4. Furthermore, heat capacity measurements and dynamic mechanical experiments performed on samples submitted to different cooling cycles allow assignment of the transition observed with these techniques around 233 K and corresponding in E.S.R. studies to the appearance of a mobile component at 273 K, to a few isolated disordered regions of the material. As the same E.S.R. behaviour is found for nitroxide doped PEO samples [35], this suggests that this transition is due to the diffusional segmental motion of the flexible aliphatic ether sequences of the polymer chain which

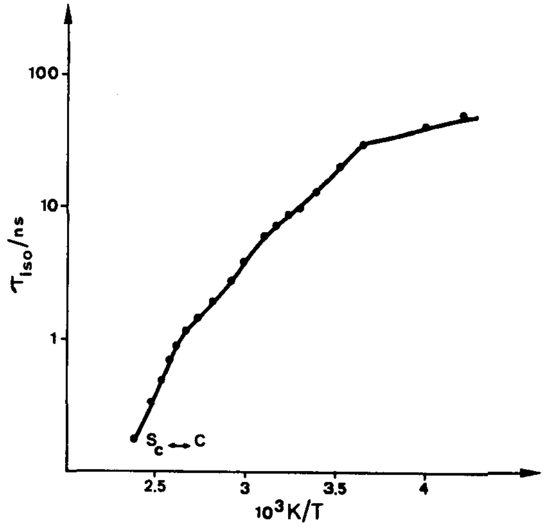


Figure 11. Isotropic rotational correlation time τ_{iso} versus $1/T$ for the Tempol probe (after [34]).

may correspond to the glass transition of the disordered glassy state. At higher temperatures, a marked increase in heat capacity is evidenced between 293 K and 323 K which is associated with the glass transition of the smectic C glassy regions of the material. In this temperature range, the solid state component of the Tempol E.S.R. spectra shifts gradually towards the mobile component and finally both components coalesce around 318 K. At still higher temperature, the slope of the arrhenian plot of τ_{iso} is changed, but the E.S.R. spectra show the characteristic features of a spin probe undergoing anisotropic rotational reorientation. The corresponding anisotropy parameter of Tempol, $N = \tau_{R\perp}/\tau_{R\parallel}$, is about 7, whereas it should be 1·35 from the molecular geometry. The temperature dependences of $\tau_{R\perp}$ and $\tau_{R\parallel}$ are plotted in figure 12. About 20 K below the crystal–smectic C transition (393 K), a premelting effect occurs, yielding a decrease in the degree of anisotropy with increasing temperature. Finally at the crystal–smectic C transition, the rotation of Tempol is temporarily isotropic. A further increase in temperature results in a marked change of the E.S.R. spectral shape: above 400 K the low-field line is sharper than the centre field line. This unusual behaviour can be interpreted by considering that the orientation of the anisotropic diffusion axis with respect to the nitroxide radical magnetic axes changes upon passing through the crystal–smectic C transition. This means that the fastest rotational motion of the Tempol probe does not occur about the same axis, that may be due to the lower constraints in the smectic C phase compared to the crystal state. Finally, it is worth noting that ^{13}C solid state N.M.R. studies [32] have shown that at the crystal–smectic C transition, the width of the aromatic carbon line decreases sharply and the associated chemical shift anisotropy change indicates a rotation of the phenyl rings around the C_1–C_4 axis in the mesophasic state. However, such a motion does not alter the mean orientation of the mesogenic groups.

In spite of the partial experimental investigations performed on the dynamic behaviour of this main chain polymer, this example clearly illustrates the improved understanding on a molecular level which arises from a combination of different spectroscopic techniques.

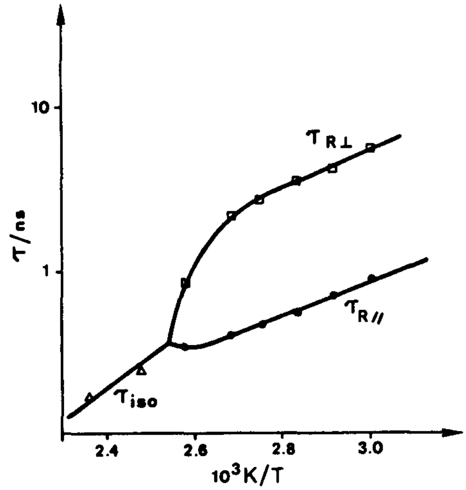


Figure 12. Correlation times $\tau_{R\parallel}$, $\tau_{R\perp}$ and τ_{iso} versus $1/T$ for the Tempol probe (after [34]).

6. Conclusion

We have discussed in this article the specific problems encountered with liquid crystal polymers, i.e. the difficulty in orientating the samples, in particular with main-chain polymers, and the occurrence of a glass–liquid transition. From the results obtained both on side-chain and main-chain liquid crystal polymers, it clearly appears that spectroscopic techniques such as ^{2}H and ^{13}C N.M.R., E.S.R. and dielectric relaxation can provide information on molecular motions occurring in these ordered phases. However, it is worth noting that a deep analysis of the results on a molecular scale requires oriented samples. In spite of the experimental difficulty in realising such an orientation of the material, the benefit which is obtained fully justifies the effort. Furthermore, the combined experiments using different techniques are the only way to achieve a molecular description of the dynamics of the system studied. Though ^{13}C and ^{2}H N.M.R. appear to be the most attractive methods, yielding information on the dynamic behaviour of the different groups in the molecule, complementary data obtained from other techniques are required to analyse the N.M.R. relaxation measurements when taking into account the different types of rotational motions which can participate to the observed relaxation (intramolecular motions, diffusional motions, orientation director fluctuations or slow relaxations of local structures).

Although in the field of liquid crystal polymers, only a few partial investigations have been performed so far, they appear very promising and a deeper insight into the dynamics of these materials should be reached in the near future.

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